STRENGTHENING MATERIALS, STRENGTHENING LAMINATES, AND COMPOSITES COMPRISING THESE STRENGTHENING MATERIALS

The present invention relates to strengthening materials suitable for use as reinforcement in composites and to strengthening laminates comprising a stack of said strengthening materials. In addition, the present invention relates to composites and/or modelled composites comprising said strengthening materials and a method for the production of composites. The present invention further relates to the use of a knit for the production of composites.

Composites or assembled multilayer structures are applied in the production of for instance boats, aircraft, cars, junction boxes, bathtubs, telephone poles, tubes, profiles and so on. Owing to their mechanical strength, relatively light weight, ability to be modelled, stiffness and resistance to for instance corrosion, composites represent an attractive alternative to for instance metal or stone.

The layers from which a composite is constructed are generally single layers of plastic, fibre, glass and/or other materials depending on the desired application.

These layers in a composite can be subdivided into for instance layers which are intended to strengthen or reinforce a composite such as strengthening layers, layers intended to provide a composite with the desired thickness or the desired volume, such as thickness-providing layers, and other layers such as covering layers, for instance for an improved protection, wear resistance, surface structure and so on, and/or finishing layers, such as for instance a paint layer or antistatic layer. A number of the above-mentioned functions may also be combined in one layer, such as for

instance a strengthening layer which also serves to prevent or reduce wear.

Composites, and particularly modelled composites, are traditionally manufactured by applying the different singular layers layer by layer, optionally in a mould, until the desired composite is formed.

This production method is however harmful to health due to the use of toxic chemicals and due to the vapours released during curing an applied layer. In addition, this method is relatively time-consuming and not sufficiently reproducible in that for instance local irregularities may occur and/or cracks in the applied layer, such as for instance during curing. This traditional manufacturing is therefore unable to provide composites of a constant quality. This method is moreover very labour intensive and time-consuming.

These problems can be wholly or partially resolved by making use during the production of composites of so-called strengthening materials as described in the European patent EP 0 873 441.

These strengthening materials comprise at least one singular thickness-providing layer of a knit of glass fibre and at least one strengthening layer connected to the thickness-providing layer, wherein the thickness-providing layer has less weight per surface area than the strengthening layer.

These strengthening materials are particularly suitable for use in the production of modelled composites owing to their excellent deformability, locally of more than 100%.

A typical production method for providing a composite, wherein use is made of the strengthening material according to EP 0 873 441, comprises of arranging the

strengthening material in a mould and subsequent modelling thereof by applying for instance a pressure or a vacuum. The final composite is obtained by for instance curing resins, such as for instance polyester resins, which are impregnated in the knit of the thickness-providing layer and/or the strengthening layers either before, or during, or after modelling of the strengthening material.

There are however a number of drawbacks associated with the use of the strengthening materials as described in EP 0 873 441.

Firstly, the use of a knit of glass fibre as thickness-providing layer results in a relatively high weight of the final composite. This is undesirable because, when composites are used as car components, body armour, sporting articles, and aircraft parts, the objective is to obtain the lightest possible composite.

Simply reducing the weight by applying a less compact knit of glass fibre in the thickness-providing layer is no solution here because the thickness-providing layer hereby becomes too thin and/or allows no or little resin transport during modelling and/or impregnation. In addition, this would also cause a reduction in the flexural stiffness of the cured composite laminate.

The relatively compact structure of the knit of glass fibre in the thickness-providing layer has the further drawback that the resin transport through this layer proceeds relatively slowly. This has an adverse effect on the duration of the production of a composite. It also limits the type of resin that can be used, since relatively fast-curing resins will already cure before a uniform distribution has been obtained in the strengthening material.

It is therefore an object of the present invention to provide a strengthening material which makes it possible to

provide relatively light composites and/or modelled composites which are as strong and/or stiff compared to the composites obtained by making use of the strengthening materials known from the prior art.

It is a further object of the present invention to provide stronger and/or stiffer composites and/or modelled composites which are stronger and/or stiffer compared to the composites with a comparable weight obtained by making use of the strengthening materials known from the prior art.

It is also an object of the present invention to provide a strengthening material which retains its thickness or volume sufficiently during modelling and/or impregnation.

It is an additional object of the present invention to provide a strengthening material in which the resin transport takes place relatively more rapidly and more uniformly during impregnation compared to the resin transport in the strengthening materials known from the prior art.

It is also an object of the present invention to provide a strengthening material which can be combined with more types of resin than is possible at this moment compared to the types of resin which can be used in combination with the prior art strengthening materials.

The above stated objectives are achieved with a strengthening material suitable for use as reinforcement in composites, comprising at least one singular thickness-providing layer in the form of a knit of glass fibre which knit comprises at least one monofilament, and at least one singular strengthening layer connected to the singular thickness-providing layer.

By using a knit of glass fibre comprising a monofilament it is possible to achieve a considerable weight-saving in comparison with the use of a knit solely of glass fibre.

The knit according to the present invention has at the same time a greater resistance to pressure or vacuum, so that the strengthening material retains its thickness to a greater extent during the modelling and/or impregnation when compared to knits solely of glass fibre. As a consequence, greatly improved strength will be provided with the thickness providing layer according to the present invention as compared to a knit of glass fibre of the same weight, thus resulting in a stronger reinforcement material with the same with weight.

In addition, a better resin transport is obtained by applying the monofilament, whereby the resin will spread more rapidly and more uniformly in the knit.

In contrast to glass fibre, a monofilament consists of one filament, usually of a plastic material. Examples of such plastic materials are polyethylene, polyester, polypropylene and polyamide, although other plastic materials are also possible. Preferred plastic materials are polyester and polyethylene, more preferred is polyethylene

Compared to glass fibres, monofilaments provide a greater stiffness at an equal or lower specific weight. This has the result that a significant weight-saving can be realized by using monofilaments in the singular thickness-providing layer.

The knit of the singular thickness-providing layer, such as for instance a flat knit or other type of knit as long as a maximum thickness is provided per weight per surface area, is obtained by processing glass fibre, such as glass filament and/or glass yarn, together with one or more monofilaments to form one cohesive spatial pattern, wherein use is made of knitting techniques which are known in the prior art, such as for instance by making use of the double flatbed knitting technique.

The spatial pattern, the density, the composition, the type of monofilament, the type of glass fibres and the knitting technique used depend on the application of the strengthening material according to the present invention. Some considerations determining this are the desired density, the desired stiffness, the desired thickness, the desired compression strength, and combinations of these properties.

The singular thickness-providing layer of the strengthening material according to the present invention preferably has a thickness of 0.5 to 20 millimetres, such as 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, of 20 millimetres. Optimal results are obtained with a thickness of the singular thickness-providing layer of 1 to 10 millimetres, such as 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 millimetres.

In addition, the singular thickness-providing layer of the strengthening material according to the present invention preferably has a weight of 25 to 1500 g/m^2, such as 25, 50, 75, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, or 1500 g/m^2.

It is recommended that the singular thickness-providing layer of the strengthening material according to the present invention has a weight of 25 to 1000 g/m^2, such as 50, 74, 100, 150, 200, 300, 400, 500, 600, 700, 800, 900 or 1000 g/m^2.

The singular strengthening layer according to the present invention, usually in the form of a non-woven, a woven fabric or a membrane, can be any material which imparts a mechanical strength or a reinforcement to the strengthening material according to the present invention.

Examples of such materials are glass fibre, aramid, carbon, basalt, ceramic, twintex, mixtures of glass and thermoplastics, flax, natural fibres, or combinations hereof.

The strengthening material according to the present invention is finally obtained by connecting at least one singular strengthening layer to the singular thickness-providing layer.

Many techniques are known which can be used to form such a connection between the singular thickness-providing layer and the singular strengthening layer. Prferred examples hereof are knitting techniques such as the Rachel technique, sewing techniques such as are used in stitching machines in the clothing industry, needle punching techniques such as are used in the textile industry for manufacturing needle felt, and/or combinations thereof.

It is particularly recommended in the strengthening material according to the present invention that the singular thickness-providing layer has less weight per unit of volume than the singular strengthening layer.

The reason for this is that the flexural stiffness of a final composite also depends on the distance between the different layers in a composite, such as for instance the strengthening layers. It is generally the case that the greater this distance, the greater the stiffness of the final composite.

In the strengthening material according to the present invention this distance is provided by the singular thickness-providing layer. Partly with a view to the weight of the final composite, it is therefore advantageous if this thickness-providing layer provides the greatest possible thickness at the lowest possible weight.

According to a preferred embodiment, the strengthening material according to the present invention comprises at least two singular strengthening layers connected to one singular thickness-providing layer in the form of a knit of glass fibre and at least one monofilament,

wherein the singular thickness-providing layer is situated between the two singular strengthening layers. This embodiment thus provides a strengthening material comprising a singular strengthening layer - a singular thickness-providing layer - a singular strengthening layer.

This construction of the strengthening material according to the present invention provides the advantage that composites can be manufactured in one step which combine great strength with a low weight.

The advantageous properties of the above described strengthening materials are obtained by a combination of a knit of glass fibre comprising at least one monofilament and at least one strengthening layer.

It will be apparent to the person with ordinary skill in the art that these properties are also obtained if a plurality of these strengthening materials are stacked to form a woven fabric or laminate, wherein the singular strengthening materials are mutually connected, using for instance the above described techniques such as knitting techniques, sewing techniques, needle punching techniques and/or combinations thereof, or using adhesion techniques such as chemical adhesion.

The present invention therefore also relates to a stacked strengthening material or strengthening laminate, comprising a stack of two or more of the strengthening materials according to the present invention.

The above described strengthening materials can be used for the production of composites, which will result in an advantageous lower weight of these composites. The present invention therefore also relates to a composite, and in particular a modelled composite, comprising a strengthening material as described above.

The present invention also relates to a method for the production of these composites, comprising of forming a strengthening material according to the present invention into a desired shape, impregnating the strengthening material with a resin, and allowing the resin to cure.

Owing to the surprising properties, and especially the improved resin transport, of the knit of glass fibre and monofilament in the thickness-providing layer, the duration of this method is considerably shortened compared to the analogous methods known from the prior art.

For reasons already stated above, the present invention also relates to the use of a knit of glass fibre and at least one monofilament for the production of composites.

The present invention will be further elucidated with reference to the following examples, which are only given by way of illustration and are not intended to limit the invention in any way whatsoever.

EXAMPLES

Comparative example 1

A strengthening material was produced consisting of three layers which were mutually connected according to the Rachel technique (for instance with a maliwatt machine from the Karl Mayer company), wherein use was made of a **knitted net** (weight 8 g/m^2) of fine-textured polyester filament of 167 dtex.

The used middle layer, or thickness-providing layer, is a flat knit composed of a glass filament of glass yarn 136 tex. The middle layer or thickness-providing layer has a thickness of about 4 mm and a weight of about 900 g/m^2.

Adhered on both sides to this middle layer or thickness-providing layer was a glass mat (strengthening layer), consisting of cut glass fibres of 50 mm length and a thickness of 25 tex, and a weight of 500g/m^2.

The total weight of the strengthening material expressed in weight/m^2 is 500 + 900 + 500 + 8 = 1908 g/m^2. The total thickness of the obtained strengthening material was about 5 mm.

Comparative example 2

In similar manner as described in comparative example 1, a strengthening material was produced consisting of three layers, the middle layer or thickness-providing layer (900 g/m^2) of which consisted of a knit of glass filament and glass yarn, and the two outer layers or strengthening layers (450 g/m^2) consisted of a glass mat.

The total weight of the strengthening material expressed in weight/m^2 is 300 + 900 + 300 + 8 = 1508 g/m^2. The total thickness of the obtained strengthening material was about 4.5 mm.

Example 1

A strengthening material according to the present invention was produced consisting of three layers mutually connected according to the Rachel technique (for instance with a maliwatt machine from the Karl Mayer company), wherein use was made of a knitted net (weight 8 g/m^2) of fine-textured polyester filament of 167 dtex.

This strengthening material can be designated as a "sandwich" construction, such as for instance a honeycomb, wherein the middle layer serves as spacer or thickness-providing layer between the two outer layers, the main function of which is to provide strength or reinforcement.

The used middle layer or thickness-providing layer is a flat knit composed of a glass filament, glass yarn 136 tex, and a polyethylene filament (PE), 33 tex monofilament, in a ratio of 136 glass to 33 PE. The middle layer or thickness-providing layer has a thickness of about 4 mm and a weight of about 280 g/m^2.

Adhered on both sides to this middle layer or thickness-providing layer was a glass mat (strengthening layer), consisting of cut glass fibres of 50 mm length and a thickness of 25 tex, and a weight of 500 g/m^2.

The obtained strengthening material is deformable and permits stretch of more than 75%. The total weight of the strengthening material expressed in weight/m^2 is 500 + 280 + 500 + 8 = 1288 g/m^2. The total thickness of the obtained strengthening material is about 4.8 mm.

Example 2

In similar manner as described in example 1, a strengthening material was produced consisting of three layers, the middle layer or thickness-providing layer of which consisted of a knit of glass filament, glass yarn 136 tex, and a polyethylene filament (PE), 33 tex monofilament, in a ratio of 136 glass to 33 PE.

The middle layer or thickness-providing layer has a thickness of about 4 mm and a weight of about 280 g/m^2. The two outer layers or strengthening layers (450 g/m^2) consisted of a glass mat. The total weight of the strengthening material expressed in weight/m^2 is 450 + 280 + 450 + 8 = 1188 g/m^2. The total thickness of the obtained strengthening material was about 4.7 mm.

Example 3

In similar manner as described in example 1, strengthening materials 3a to 3k according to table 1 were produced consisting of three layers, the middle layer or thickness-providing layer of which consisted of a knit of glass filament, glass yarn 136 tex, and a polyethylene filament (PE), 36 tex monofilament. All strengthening materials had a glass polyethylene (PE) ratio of 1 thread glass to 3 or 4 monofilaments polytheylene and a total thickness varying in the range of 4 to 5 mm. The weights of the thickness providing layers and the strengthening layers are depicted in Table 1.

Table 1

Strengthening material	Weight thickness providing layer (g/m²)	Weight strengthening layers ((g/m²)	Total weight (g/m²)
3a	210	200	618
3b	210	300	818
3c	210	450	1118
3d	210	600	1418
3e	250	300	658
3f	175	300	783
3g	250	450	1158
3h	210	225	668
3i	280	450	1188
3j	300	450	1208
3k	200	450	1108

Example 4

The thickness under a determined pressure of the strengthening material according to example 1 and comparative example 1 were compared, and it was found that strengthening material according to the present invention displayed about 7% less compression at the same pressure. The strengthening materials were compared under different pressures (vacuum) and the results hereof are shown in table 2.

Table 2

Type of strengthening material	**Weight/m²**	**Thickness at a pressure of 0.5 kg/cm²**	**Thickness at a pressure of 1 kg/cm²**
Comparative example 1	1908g	2.2 mm	2.0 mm
Example 1	1288g	2.35 mm	2.15 mm

Table 2 shows that the strengthening material according to the present invention provides a weight-saving of 620 g/m^2, and in addition provides less compression under pressure, which will result in a thicker composite and a better resin transport.

Improved resistance to compression as compared to similar strengthening materials comprising a thickness providing layer of only a glass knit of the same weight were obtained using the strengthening materials 3a to 3k according to example 3.

Example 5

A composite, in this case a helmet, was manufactured using the so-called "vacuum technique closed mould system". In summary, a first film was placed in a mould and the strengthening material according to example 2 and a polyester

resin were placed thereon. A second film was then placed on the strengthening material according to example 2 and, after the edges of the first film and the second film were closed, a vacuum was created between the mould and the first foil and between the first and the second film.

Under the influence of the vacuum the strengthening material was modelled as according to the shape of the mould and the resin was simultaneously pressed to the outer ends of the strengthening material. After impregnating the resin in the strengthening material, i.e. through the thickness-providing layer and into the strengthening layers, and after curing of the resin, a modelled composite was obtained in the form of a helmet.

This method was repeated wherein use was made of the strengthening material according to comparative example 2 instead of the strengthening material of example 2.

The time required for a full impregnation of both strengthening materials was measured, and this is shown in table 3.

Table 3

strengthening material	Weight/m^2	impregnation time
Comparative example 2	1508 g	23 minutes
Example 2	1188 g	17 minutes

Table 3 shows that the strengthening material according to the present invention provides at least three advantages: 1) a shorter production time, 2) a stronger composite (900 g/m^2 against 600 g/m^2 strengthening material) with a lower weight (1188 g/m^2 against 1508 g/m^2), and 3) a saving of raw materials and hence a cheaper product.

Reduced impregnation times as compared to strengthening materials comprising a thickness providing layer of a glass knit of the same weight were obtained using the strengthening materials 3a to 3k according to example 3.

Example 6

A composite was manufactured using the so-called "injection technique closed mould system". In summary, the strengthening material according to example 2 was placed in a closed mould, in this case a mould for a helmet, with a cavity of 3 mm. After the mould had been closed, polyester resin was injected under pressure. After impregnation of the resin through the thickness-providing layer and into the strengthening layers, a composite in the form of a helmet was obtained after curing.

This method was repeated wherein use was made of the strengthening material according to comparative example 2 instead of the strengthening material of example 2.

The time required for a full impregnation of both strengthening materials was measured, and this time is shown in table 3.

Table 4

strengthening material	Weight/m^2	impregnation time
Comparative example 2	1508 g	15 minutes
Example 2	1188 g	<10 minutes

Table 4 shows that the strengthening material according to the present invention provides at least three advantages: 1) a shorter production time, 2) a stronger composite (900 g/m^2 against 600 g/m^2 strengthening material)

with a lower weight (1188 g/m^2 against 1508 g/m^2), and 3) a saving of raw materials and hence a cheaper product.